APPENDIX - IV

MAHARSHI DAYANAND SARASWATI UNIVERSITY, AJMER

Format for Outline of Proposed Research work
(to be supplied in Six copies)

1. Nameof Scholar (In English) Devendra kumar Mahawar
   (In Hindi) देवेन्द्र कुमार महावर
2. Title of the Research Work :
   (In English) Theoretical Studies On Nano Clusters and their role as potential Catalysing Agent
   (In Hindi) नैनो क्लस्टर का सैद्धान्तिक अध्ययन एवं इनकी प्रभावी उत्प्रेरक के रूप में भूमिका
3. Location
   a. Institution/Department where the work is to be done Govt. P.G. College Tonk
   b. Geographical area of Investigation, if any.
4. Introduction Importance of Proposed Investigation, Objectives. P 1-3
5. Review (Work already done on the subject of proposed Research Study.) P-3
6. Research Gaps identified in the proposed field of investigation. (Based on the review) P-5
7. Major Hypothesis, if any. P-5
8. Research Methodology. P-6
9. List of References cited. P-7

5/12/12

Signature of the Candidate with date

Outline Approved.

Name and Signature of supervisor with date & seal.

5/12/12

Dr. Manoj Sikarwar

[redacted]

Scanned with CamScanner

APPENDIX - VI

MAHARSHI DAYANAND SARASWATI UNIVERSITY, AJMER

Certificate By Supervisor

Certified that :

1. I am willing to guide the research work of Shri/Km./Smt. Devendra Kumar Mahawar on the above subject if he/she is registered for Ph.D.
2. To the best of my knowledge, the subject selected has not been studied and is not being studied so far in any University.
3. The subject is of sufficient scope to keep the candidate engaged for two years.
4. The subject will lead to a valuable contribution. I have seen and approved the outline of proposed research work submitted by the candidate.
5. I have ..... NIL ..... (give numbers) Research candidates registered under my supervision and the serial number of this candidate whose application is being forwarded for registration is ..... 01 ..... (give the serial number)
6. The candidate is not in a close relation (the term of close relation is defined in the examination ordinance of the University)

Signature of the Supervisor with date

Certified that the available facilities will be extended to Shri/Km./Smt. Devendra Kumar Mahawar for research work if he/she is registered for Ph.D.

10.12.12

Signature of the Principal/ Director of the Institution with date

---

Signature of the Head, Department with date

Scanned with CamScanner

Synopsis for Registration of Ph.D. in Chemistry

Title: Theoretical studies on Nano Clusters and their role as potential catalyzing agent

Introduction

Nanocatalysis is one of the most exciting subfields to have emerged from nanoscience. Its central aim is the control of chemical reactions by changing the size, dimensionality, chemical composition and morphology of the reaction center and by changing the kinetics using nanopatterning of the reaction centers. This approach opens up new avenues for atom-by-atom design of nanocatalysts with distinct and tunable chemical activity, specificity, and selectivity. The interest in nanoscale materials arises from the fact that new properties are acquired at this length scale and, equally important, that these properties change with their size or shape. The change in the properties at this length scale is not a result of scaling factors. It results from different causes in different materials. In transition metal nanoparticles, the decrease in the particle size to the nanometer length scale increases the surface-to-volume ratio[1]. This, together with our ability to make them in different sizes and shapes, makes them potentially useful in the field of catalysis. An important reason for the interest in clusters is the size-dependent evolution of their properties[2,3,4] such as their structure. In fact, both the geometric shape and the energetic stability of clusters may drastically change with size. For example, it is known that alkali-metal clusters, with sizes of up to thousands of atoms (and also smaller clusters of Cu and Ag), conform to the jellium model in that certain nuclearities are relatively stable (the so-called *magic sizes*) due to their having filled electronic shells.[5,6] By contrast, clusters of transition metals and some main-group metals (e.g., Al, Ca, and Sr) generally exhibit magic sizes which correspond to clusters consisting of concentric polyhedral shells (*geometric shells*) of atoms, where the relative stability of a given cluster is determined by the competition between packing and surface energy effects[5,7].

Importance

Nowadays, globally increasing energy demands and growing environmental concerns have highlighted urgent issues and big challenges in exploring alternative energy sources and eliminating the emissions of carbon dioxide and toxic pollutants in our environment. Mitigating these important factors is critical for the survival of the planet and one way to tackle them is through advanced catalysis,

Scanned with CamScanner

such as photocatalysis, catalytic bioconversion, CO_2 conversion, CO oxidation and steam reformation, etc. Nanoscience and nanotechnology has played a key role in developing these processes and nanocatalysis research has undergone explosive growth in the past decades, utilizing nanoscale materials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. A central aim of nanocatalysis research is to develop effective catalysts with sole selectivity, extremely high activity, low energy consumption, and a long lifetime. This objective can be achieved only by precisely controlling the size, dimensionality, morphology, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nanocomponents for the catalysts. To this end, researchers worldwide have invested tremendous effort on controlled fabrication of nanocatalysts with distinct and tunable chemical activity, specificity and selectivity. Although these studies have contributed significantly to our fundamental understanding of catalysis, there are still big challenges involved in controlling their nanoscale structures at an atom-by-atom level and on the understanding their synthesis-structure-performance relationships.

Many interesting phenomena involving nanomaterials have been observed during the past two decade due to their unique structural, mechanical, and electrical properties. The increasing availability of highly sophisticated experimental techniques combined with the high quality electronic structure calculation methods have improved the understanding of the complex nature of these nanomaterials and properties. One of the most recent observations is that of gold based catalysis at the nanoscale. It is well known that while the bulk phase of the gold is inert, the gold nanoparticles of size around 1-5 nm has been found to be an excellent catalyst for many organic and inorganic reactions. Among these chemical reactions, the interesting catalytic reactions are the oxidation of carbon monoxide at 200 K and activation of oxygen molecules. The adsorption of molecules on small metal clusters in the gas phase is an active field of experimental and theoretical research. In view of the importance of these chemical reactions, in the proposed work, we would like to do a theoretical study on the structure and electronic properties of various nano clusters of transition elements and their role as potential catalyzing agents and also other nano assemblies like carbon nano tubes.

Another interesting field is related with organic solar cells (OSCs) exhibiting tremendous potential in the world's energy strategy. The achievement of high power conversion efficiencies (PCEs) can accelerate their practical applications. To maximise the PCEs of OSCs, it requires a full understanding of the elementary processes for the conversion of solar energy into electricity and finding optimal combinations of donor-acceptor materials in terms of optical, electronic and morphological properties, which can be obtained through the judicious selection of

Scanned with CamScanner

existing and new materials. Computational modelling plays an essential role in understanding and predicating the behaviour of OSC active materials at the molecular level.

Objective

In the proposed research work we will take up the theoretical study of nano clusters and possibly we also propose to investigate structural, electronic, optical, and photochemical properties of nanostructure solar cells and molecular solar energy conversion processes using first principles computational modelling techniques.

Thus our objectives are as follows:

1. Theoretical study of structure and electronic properties of different sized nano Clusters of Ag, Cu, Au and also of other possible candidates, after obtaining equilibrium geometries by energy optimization at the different level and examining their stability.
2. Catalytic application of nanoclusters supported on oxides and on other surfaces for CO oxidation and other oxidation process used in heterogeneous catalysis.
3. Theoretical investigation of solar cells and solar energy conversion using first principles computational modelling techniques.

Review of Literature

Although bulk phase Gold has long been known as the chemically inert metal, it was the report of Haruta et al. [8] that showed that nanosized gold clusters can be catalytically active. A wide variety of chemical reactions, e.g. CO oxidation[9], epoxidation[10, 11], C-C bond formation[12], water gas shift[13] and selective hydrogenation/reduction[14] are reported to be catalysed by supported gold clusters. Especially, the most notable is the environmentally important reaction of oxidation of CO to CO_2 at temperatures far below room temperature.

Whetten's group[15] who studied O_2 adsorption on Au_n^- clusters found that Au_n^- clusters with odd n do not adsorb O_2 and that Au_n^- clusters with even n will only adsorb one O_2 molecule. The interest in oxygen chemistry on Au_n clusters is heightened by the recent discovery that very small Au clusters are good oxidation catalysts.

The direct vapor-phase epoxidation of propene to propene-oxide in the presence of molecular oxygen and hydrogen over gold catalysts supported on Ti-incorporated silica materials prepared by different methods have been reported by A.K. Sinha et al.[10]

Scanned with CamScanner

The properties of the alkali metal clusters have been investigated by K. R. S. Chandrakumar's group[16-17] using ab initio electronic structure calculations, with special reference to their structural evolution and the size dependence of several reactivity descriptors.

In the past two decades, great attention has been paid for the direct synthesis of H_2O_2 from H_2 and O_2 with Pd and Au-based catalysts.[18-22] Olivera et al.[21] predicted that gold would be a better catalyst for the direct synthesis of H_2O_2 than Pd, Pt, and Ag. Subsequent experiments did reveal that highly dispersed Au nanoparticles are very selective and active for the synthesis reaction.[22, 23] Theoretical investigation of the formation of hydrogen peroxide from H_2 and O_2 over anionic gold clusters Au_n^- (n = 1-4) has been proposed by Fang Wang et al.[24]

Structure, bonding, and linear optical properties of a series of silver and gold nanorod clusters whose structures are of cigar-type has been performed by Meng-Sheng Liao et al.[25] using DFT/TDDFT.

Greg Mills[26] used density functional theory to examine the binding of O_2 to Au_n and Au_n^- clusters (n= 2–5).

Theoretical investigation on the structure and electronic properties of hydrogen- and alkali-metal-doped gold clusters and their interaction with CO, an enhanced reactivity of hydrogen-doped gold clusters has been reported recently by Naresh K. Jena et al.[27]

Ab initio studies on the electronic structure and properties of Aluminum hydrides viz., *closo* (Al_nH_{n+2}), *nido* (Al_nH_{n+4}), and *arachno* (Al_nH_{n+6}) that are analogues of boron hydrides has been done by K. Srinivasu et al.[28]

The replacement of Au atom with a H-atom in a gold cluster can lead to considerable enhancement in its reactivity. The H-doped gold cluster reduces the barrier height for the environmentally important CO oxidation reaction as compared to the pristine cluster.[29]

Rhitankar Pal et al.[30] reported spectroscopic evidence of two modes of O_2 activation by the small even-sized Au_n^- clusters, superoxo and peroxo chemisorption. Their work shows that there is a superoxo to peroxo chemisorption transition of O_2 on gold clusters at Au_8^-, $O_2Au_n^-$ (n = 2, 4, 6) involves superoxo binding and n = 10, 12, 14, 18 involves peroxo binding, whereas the superoxo binding re-emerges at n = 20 due to the high symmetry tetrahedral structure of Au_{20}, which has a very low electron affinity.

Density functional theory study of the adsorption of nitrogen and sulfur atoms on gold (111), (100), and (211) surfaces has been reported by April D. Daigle and Joseph J. BelBruno.[31]

H. M. Lu and X. K. Meng[32] proposed a theoretical model to calculate catalytic activation energies of platinum nanoparticles of Different sizes and shapes.

Scanned with CamScanner

Recently, Naresh K. Jena et al.[33] reported Density functional theory (DFT) based study that explores the possibilities of using complexes of DNA bases.

Following these initial reports of the reactivity of nanoparticles, the stage has been perfectly set for the study of nanoscale catalysis leading to an upsurge of activities on structural aspects, electronic properties of clusters, and their potential applications in nanocatalysis.[34-51]

Research Gaps

Sub-nanometer sized metal clusters, with dimensions between metal atoms and nanoparticles have attracted more and more attention due to their unique electronic structures and the subsequent unusual physical and chemical properties. There is a big need to use metals clusters of gold, especially the alkanethiolate monolayer protected clusters (MPCs) and other alternatives, to investigate them extensively. Also silver and copper nanoclusters which are of enormous interest mainly due to their excellent photo luminescent properties make them a challenging task for finding more structural characteristics, particularly optical, catalytic, electronic and magnetic properties and the related technical applications of the metal nanoclusters.

In study of solar cells particular, systematic investigations of light-harvesting, and efficient charge separation at interfaces through ultrafast photoinduced electron transfer at interfaces have importance for fundamental understanding to the current generation in Grätzel solar cells and related solar energy conversion systems.

Major Hypothesis

It is very well known that elements of d-block show the property of complex formation due to existence of vacant or partially filled d-orbitals. The transition metals and their compounds are known for their homogeneous and heterogeneous catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes; also because the transition metal ions can exhibit variable oxidation states, they become more effective as catalysts. Platinum-group metals, e.g., Pt, Pd, Ir, Ru, and Rh, are known to effectively catalyze a large number of chemical reactions.

Most often, these metals are used as oxide-supported small particles for oxidation reactions in the chemical industry, in automotive emission control, and in energy-related technologies.[52,53]

Further, these metals are of great interest due to the fact that new properties are acquired at nano scale and, that these properties change with their size or

Scanned with CamScanner

shape. In these metal nanoparticles, the decrease in the particle size to the nanometer scale increases the surface-to-volume ratio. This, together with our ability to make them in different sizes and shapes, makes them potentially useful in the field of catalysis.

The most important reason for transition metals to be good catalysts is that they can lend electrons or withdraw electrons from the reagent, depending on the nature of the reaction. The ability of transition metals to be in a variety of oxidation states, the ability to interchange between the oxidation states and the ability to form complexes with the reagents and be a good source for electrons make transition metals good catalysts.

Research Methodology

The theoretical calculations will be done at various levels like Hartree-Fock, Density Functional Theory (DFT), Second order Møller–Plesset perturbation theory (MP2), second-order approximate coupled cluster (CC2), using different basis set and different density functional based exchange-correlation methods like DFT-RI using different functionals. Single point energy calculations and energy optimization will be done at different levels using different basis set and with different density functionals. For this one of the suitable software code like GAMESS, VASP, TURBOMOLE etc. will be used.

Scanned with CamScanner

List of References:

(1) Burda, C.; Chen, X.; Narayanan, R.; Mostafa A. El-Sayed *Chem. Rev.* **2005,** 105, 1025-1102.

(2) Johnston, R. L. *Atomic and Molecular Clusters*; Taylor and Francis: London, **2002.**

(3) Jortner, J. *Z. Phys. D* **1992**, *24*, 247.

(4) Johnston, R. L. *Philos. Trans. R. Soc. London A* **1998**, *356*, 211.

(5) Baletto, F.; Ferrando, R. *Re*V. *Mod. Phys.* **2005**, *77*, 371.

(6) De Heer, W. A. *Re*V. *Mod. Phys.* **1993**, *65*, 611.

(7) *Large Clusters of Atoms and Molecules*; Martin, T. P., Ed.; Kluwer: Dordrecht, **1996.**

(8) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405–408.

(9) M. Haruta, *Catal.Today* **1997**, 36, 153.

(10) Sinha, A.K.; Seelan, S.; Tsubota, S.; Haruta, M. *Top. Catal.* **2004**, 29, 95.

(11) Nijhuis, T.A.; Visser, T.; Weckhuysen, B.M. *J. Phys. Chem. B.* **2005**, 109, 19309.

(12) Tsunoyama, H.; Sakurai, H.; Ichikuni, N.; Negishi,Y.; Tsukuda, T. *Langmuir* **2004**,20, 11293.

(13) Bond, G.C. *Gold Bull.(London, U.K.)* **2009**, 42, 337.

(14) McEwan, L.; Julius, M.; Roberts, S.; Fletcher, J.C.Q. *Gold Bull.(London, U.K.)* **2010**, 43(4),298.

(15) Salisbury, B.E.; Wallace, W.T.; Whetten, R.L. *Chem.Phys*. **2000**, 262, 131.

(16) Chandrakumar, K. R. S.; Ghanty, T. K.; Ghosh S. K. *J. Phys. Chem. A* **2004**,108, 6661-6666

(17) Chandrakumar, K. R. S.; Ghanty, T. K.; Ghosh S. K. *J. Chem. Phys.* **2004**,120, 6487.

(18) Dissanayake, D. P.; Lunsford, J. H. *J. Catal.* **2002**, *206*, 173-176.

(19) Choudhary, V. R.; Samanta, C.; Jana, P. *Appl. Catal. A* **2007**, *317*, 234-243.

(20) Zhou, B.; Lee, L. K. U.S. Patent 6,168,775, **2001**.

(21) Olivera, P. P.; Patrito, E. M.; Sellers, H. *Surf. Sci.* **1994**, *313*, 25-40.

(22) Landon, P.; Collier, P. J.; Papworth, A. J.; Kiely, C. J.; Hutchings,G. J. *Chem. Commun.* **2002**, *18*, 2058-2059.

(23) Okumura, M.; Kitagawa, Y.; Yamagcuhi, K.; Akita, T.; Tsubota, S.; Haruta, M. *Chem. Lett.* **2003**, *32*, 822-823.

(24) Wang, F.; Zhang, D.; Sun, H.; Ding, Y. *J. Phys. Chem. C* **2007,** *111,* 11590-11597.

Scanned with CamScanner

(25) Liao, M.S.; Bonifassi, P.; Leszczynski, J.; Ray, P.C.; Huang, M.J.; Watts, J.D. *J. Phys. Chem. A* **2010,** *114,* 12701–12708.

(26) Mills, G.; Gordon, M.S.; Metiu H. *Chem. Phys. Lett.* **2002,** 359,493–499.

(27) Jena, N.K.; Chandrakumar, K.R.S.; Ghosh S.K. *J. Phys. Chem. C* **2009,** *113,* 17885–17892.

(28) Srinivasu, K.; Chandrakumar, K. R. S.; Ghosh, S.K. *J. Phys. Chem. A* **2010,** *114,* 12244–12250.

(29) Jena, N.K.; Chandrakumar, K.R.S.; Ghosh S.K. *J. Phys. Chem. Lett.* **2011,** 2, 1476–1480.

(30) Pal, R.; Wang, L.M.; Pei, Y.; Wang, L.S.; Cheng Zeng, X. *J. Am. Chem. Soc.* **2012,** 134, 9438–9445

(31) Daigle, A. D.; BelBruno, J. J. *J. Phys. Chem. C* **2011**, 115, 22987–22997

(32) Lu,H. M.; Meng, X. K. *J. Phys. Chem. C* **2010,** *114,* 1534–1538

(33) Jena, N.K.; Chandrakumar, K.R.S.; Ghosh S.K. *J. Phys. Chem. C*, **2012**, 116 (32), 17063–17069

(34) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, *16*, 405–408.

(35) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301–309.

(36) Seminario, J. M.; Tour, J. M. *Int. J. Quantum Chem.* **1997**, *65*,749–758.

(37) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647–1650.

(38) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566–575.

(39) Boccuzzi, F.; Chiorino, A.; Manzoli, M.; Andreeva, D.; Tabakova, T. *J. Catal.* **1999**, *188*, 176–185.

(40) Rousseau, R.; Marx, D. *J. Chem. Phys.* **2000**, *112*, 761–769.

(41) Ha¨kkinen, H.; Landman, U. *Phys. Re*V. *B* **2000**, *62*, R2287–R2290.

(42) Gro¨nbeck, H.; Andreoni, W. *Chem. Phys.* **2000**, *262*, 1–14.

(43) Kruger, D.; Fuchs, H.; Rousseau, R.; Marx, D.; Parrinello, M. *J. Chem. Phys.* **2001**, *115*, 4776–4786.

(44) Haruta, M. *Gold Bull.* **2004**, *37*, 27–36.

(45) Meyer, R.; Lemire, C.; Shaikhutdinov, S. K.; Freund, H.-J. *Gold Bull.***2004**, *37*, 72–124.

(46) Thompson, D. T. *Top. Catal.***2006**, *38*, 231–240.

Scanned with CamScanner

(47) Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. *Science* **2008**, *321*, 1331–1335.

(48) Lee, S.; Molina, L. M.; Lo´pez, M. J.; Alonso, J. A.; Hammer, B.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Pellin, M. J.; Vajda, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 1467–1471.

(49) Pyykko¨, P. *Angew. Chem.* **2004**, *116*, 4512–4557. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412-4456.

(50) Kim, Y. D. *Int. J. Mass. Spec.* **2004**, *238*, 17–31.

(51) K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, Van Nostrand Reinhold, New York, **1979**

(52) Handbook of Heterogeneous Catalysis; Ertl, G., Knoezinger, H., Weitkamp,J., Eds.; VCH: Weinheim, Germany, **1997**.

(53) Principles and Practice of Heterogeneous Catalysis; Thomas, J. M.; Thomas, W. J. VCH: Weinheim, Germany, **1997**

Scanned with CamScanner